OCTOBER 1966
REPORT SM-49109-Q1

DEVELOPMENT OF ONE AMPERE-HOUR HEAT STERILIZABLE SILVER-ZINC CELL

PROGRESS REPORT FOR PERIOD
1 JULY 1966 TO 30 SEPTEMBER 1966
UNDER CONTRACT NAS 2-3819

Report SM-49109-Q1

DEVELOPMENT OF ONE AMPERE-HOUR HEAT STERILIZABLE SILVER-ZINC CELL

Progress Report for Period
1 July 1966 to 30 September 1966

Contract NAS 2-3819

By:

Albert Himy

A. Himy
Senior Research Scientist

Approved by:

Carl Berger

C. Berger, Ph.D.
Head, Electrochemistry Department

MISSILE & SPACE SYSTEMS DIVISION
ASTROPOWER LABORATORY
Douglas Aircraft Company, Inc.
Newport Beach, California

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

1.0 INTRODUCTION

The objective of this program is to develop a one ampere-hour heat sterilizable sealed silver-zinc cell capable of withstanding sterilization pressure and still performing a duty cycle after 10 months' wet life.

The preliminary design was established for separators, electrodes, cell assembly, case, and cover terminals, but remains subject to modification after initial testing.

Testing was carried out on cell components: (1) mechanically, regarding the attachment of electrode leads to the terminal base, the terminal seal, and the cover-to-case seal; (2) electrically, regarding polarization data at various current densities for different systems and electrolytes.

The heat-sterilization procedure was carried out on cell components separately and in combination to determine their contribution to gas pressure build-up in a sealed system, as well as to gas composition.

Generally, the overall progress of the work in the first quarter was satisfactory.

2.0 OBJECTIVES

The prime consideration of the program is to design, fabricate, test, and evaluate a heat-sterilizable unit cell which may be used in space missions where sterilization is required, such as planetary probes and orbiters. This cell will be capable of being recharged after heat sterilization.

The following is a set of specifications around which the unit cell will be designed and built.

Nominal Voltage: 1.5 V

Nominal Capacity: 1 Ah

Load Profile: 3 mA for 72 hours followed by 2 A for two minutes. (Capacity required: 0.30 Ah)

Temperature range during transit and operation: 50°F to 85°F

Storage temperature in discharged state: 0°F to 125°F

Sterilization: As per JPL Specification XSO-30275-TST-A

Operating Life: 1 year

Design Objective: The cell shall be sealed during sterilization, transit, and operation.

Environmental Requirements:

1. Shock

   The cell shall withstand three shocks of 18 G's in each direction along each of three mutually perpendicular axes (18 shocks). The wave shape and associated time duration of the input pulse will be one of the following:

   A. Triangular pulse at 10 milliseconds time duration.
   B. Half-sine pulse at 8 milliseconds time duration.
   C. Rectangular pulse at 5 milliseconds time duration.

2. Vibration

   A resonant survey test shall be run on the cell to determine the resonant modes of the cell structure. A sweep shall be made from 5 to 16 cps at 0.368 inch DA and 16 to 200 cps at 5 G peak on each of three mutually perpendicular axes. Measurement shall be made at the point of coupling between the exciting mechanism and the cell. A notation shall be made of all resonances in each direction.

3. Acoustic Noise

The cell shall withstand a total integrated sound pressure level of 148 db, Re 0.002 micro-bar with a frequency spectrum as shown in Figure 1 for a period not less than 5 minutes.

4. Acceleration

The cell shall withstand accelerations as shown in the following schedule:

A. 7 G's acceleration for 5 minutes along the longitudinal axis in a direction corresponding to the lift-off of the transporting vehicle.
B. 3 G's acceleration in the opposite direction for 5 minutes duration.
C. 4.5 G's acceleration in both directions along mutually perpendicular axes for 5 minutes duration.

The objective of this work is to deliver five unit cells to NASA that are capable of meeting the above specifications. However, a parametric study of the current-voltage-temperature relationship will be performed to provide NASA with information about the capability of the cells for a variety of other space missions.

The unit cells will be delivered wet, discharged and sealed, but not sterilized. The sterilization shall be performed by NASA prior to use, as per JPL Specification XSO-30275-TST-A, any time within the year following the delivery of the cells.

The cells may be assembled in any configuration desired by NASA to obtain the shape and voltage necessary for the mission. A battery design study will be performed at the end of the program after getting the necessary information.

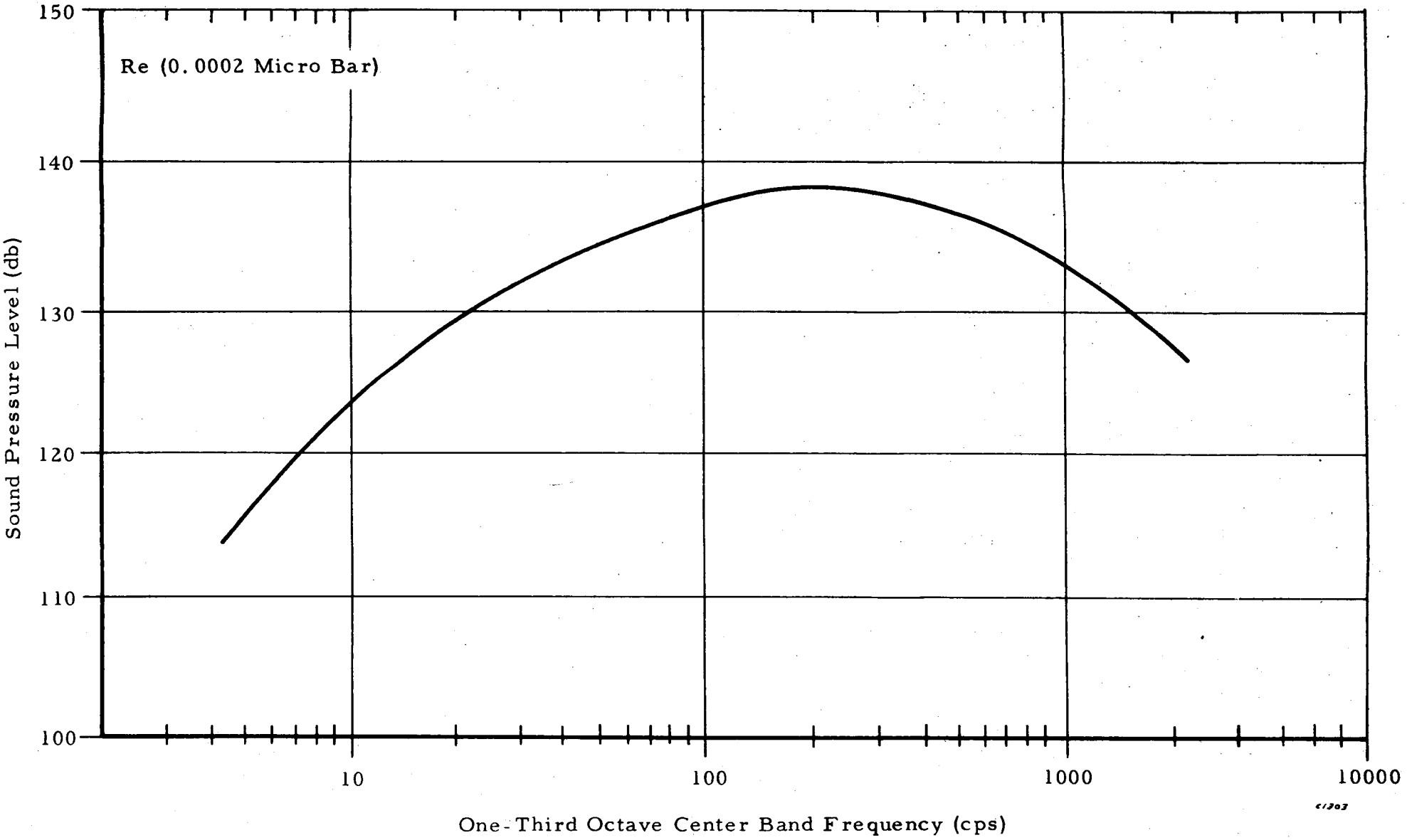


Figure 1. Acoustic Noise Frequency Spectrum

3.0 DESIGN

Each component of the cell will be considered separately and designed or selected with the prime objective of meeting the requirements of the heat-sterilization procedure.

3.1 Separators

Based on our previous experience, the inorganic separator coded 3420-09 was selected for this program as a starting point because of its high resistance to degradation in concentrated potassium hydroxide solution at 145°C for very long periods of time.

The specifications were tentatively set as follows:

Dimensions

Length:	2.030 ± 0.010 inches
Width:	1.900 ± 0.010 inches
Thickness:	0.026 ± 0.001 inch

Weight

4.0 ± 0.1 grams

Water Absorption (ratio of water pick-up, filling the pores, to the dry weight)

9.5% ± 1%

Apparent Density

2.40 ± 0.1 g/cm^3

Resistivity in 30% KOH

27 ± 3 ohm-cm

3.2 Interseparators

Interseparators are materials used on either the positive or the negative electrode or both because of their wetting characteristic, i.e., their ability to retain electrolyte and to keep the electrode constantly wetted. They also serve as cushions between the relatively rigid components (the inorganic separator and the silver electrode).

The following materials have been considered and screen-tested (see Section 4.3.3).

1. Polyamide fiber felt (Pellon Corp.)
2. Treated nylon fabric (Gelman Acropor Type AN450)
3. Polypropylene SM-91 (Kendall Mills)
4. Polypropylene EM-476 (Kendall Mills)
5. Potassium Titanate fiber sheet (KT) (Dupont)
6. Asbestos fiber sheet (Johns-Manville)
7. Astropower 4561-7* (Douglas Aircraft)

The latter is an organic-inorganic composition which has been previously developed by Astropower and which is applied as a coating on the electrode.

3.3 Electrodes

The active materials and construction types of the electrodes have been kept identical to those used in previous Astropower work. Although the design has not been finalized, electrodes were manufactured to the following specifications for all work performed to date.

3.3.1 Positive

Material: Silver powder Silpowder 130 from Hardy and Harman

Grid: Silver expanded metal 3 Ag 10 - 3/0

Lead: Silver strip 1/4" x .006" spotwelded to grid

Size: 1.500" x 1.500" (±0.005")

Area: 14.5 cm^2

Thickness: 0.025" ± 0.001"

Weight of Active Material: 4.1 ± 0.1 g

3.3.2 Negative

Material: Mix of 98% ZnO and 2% HgO

Grid and Lead: Same as positive

*Proprietary

Size: 1.500" x 1.500" ± 0.005"

Area: 14.5 cm^2

Thickness: 0.075" ± 0.002"

Weight of Active Material: 7.0 ± 0.1 g

Supporting Material: KT-20 (20 mil thick Potassium Titanate fiber sheet pressed into the plate to a thickness of about 10 mils).

3.4 Cell Assembly

The preliminary electrode assembly consists of two positive and one negative electrode. The negative electrode is sandwiched between two inorganic separators, and the edges are sealed with an epoxy resin, resulting in a wafer configuration* where the negative is tightly enclosed in a cavity. The silver electrodes are placed on each side of the negative wafer (Figure 2). All preliminary electrical and sterilization tests were conducted on cells of this type.

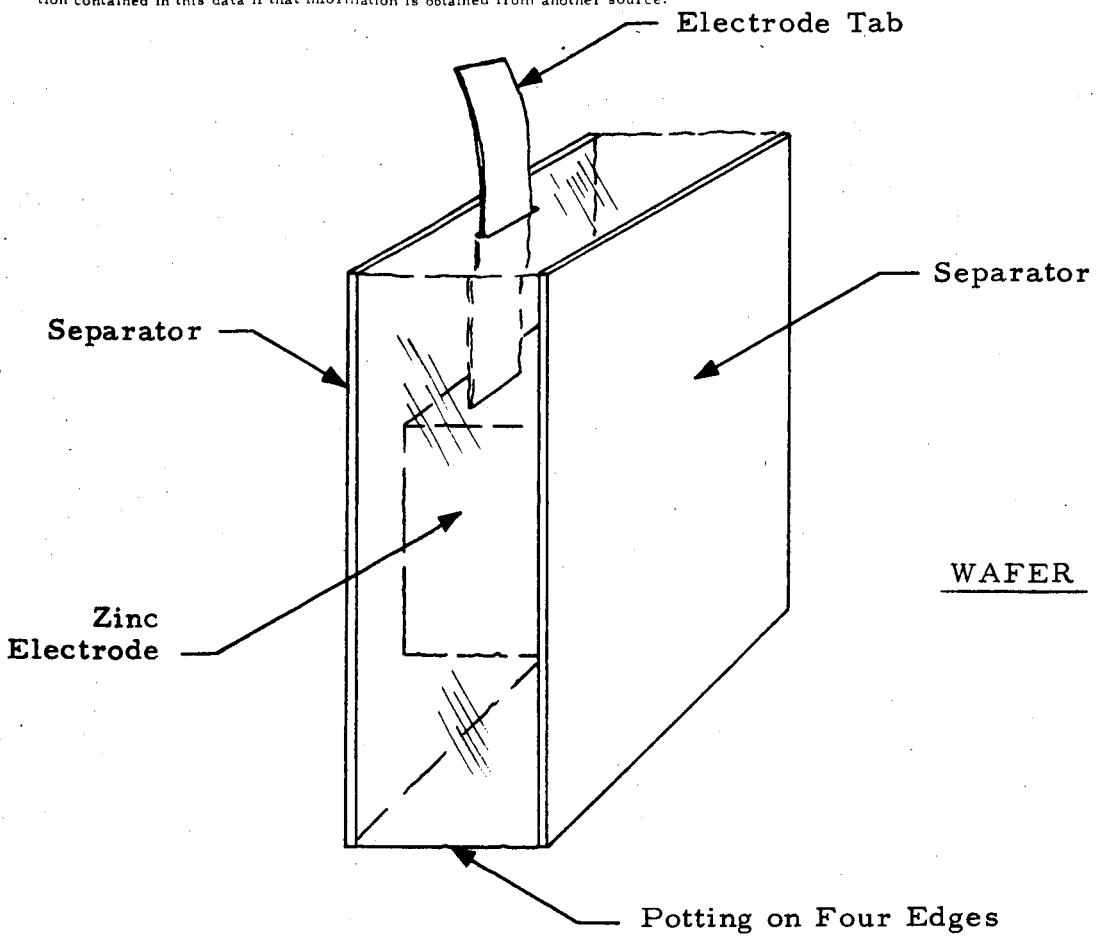
However, the cell assembly is not finalized. It may be of interest to use the one-positive and two-negative configuration, where a large excess of zinc would be more advantageous in avoiding any possiblity of zinc limiting charge, producing undesired hydrogen gassing and subsequent pressure build-up, or limiting discharge after prolonged wet stand. The electrical characteristics of the cell will not change with regard to voltage, since the current density remains constant; the single silver plate may be designed to provide at least the one Ah capacity required.

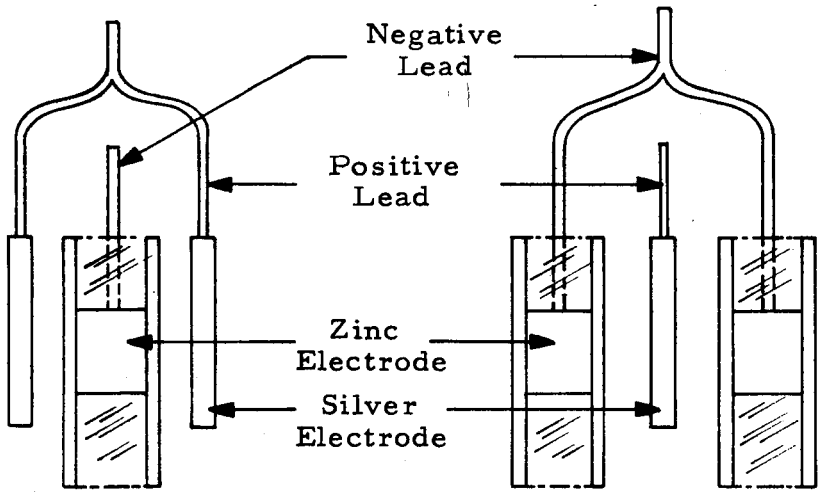
3.5 Case and Cover

For the sake of convenience and expediency, temporary design of case and cover was established and parts were fabricated from polysulfone flat stock material, grade P-1700 (Union Carbide). Eventually a mold will be required after finalization of the design.

Figure 3 shows a photograph of case and cover with terminals installed. The center hole in the cover is for electrolyte filling and for attaching a pressure gauge.

*Proprietary





Wafer Assembly

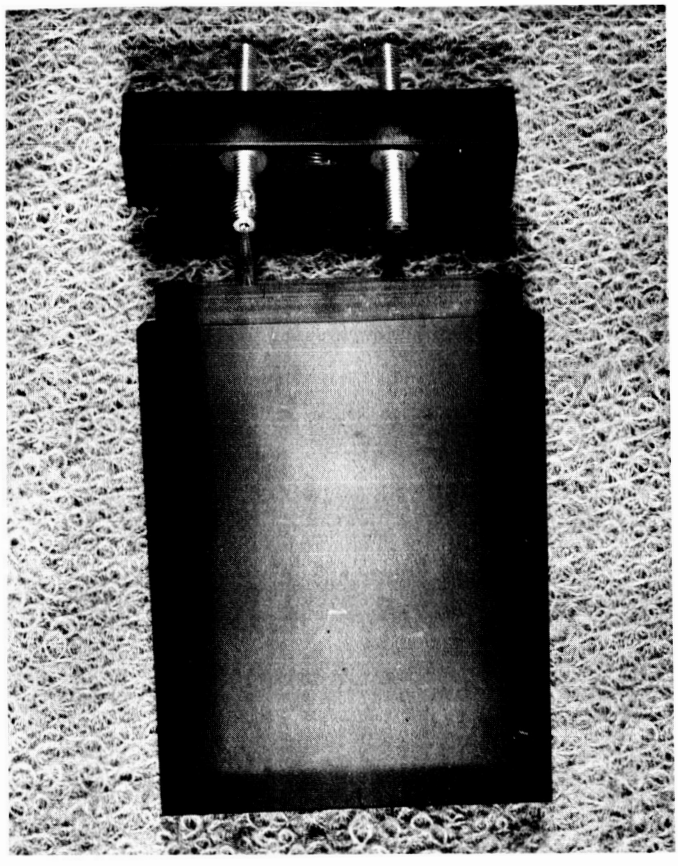
2 Positives
1 Negative

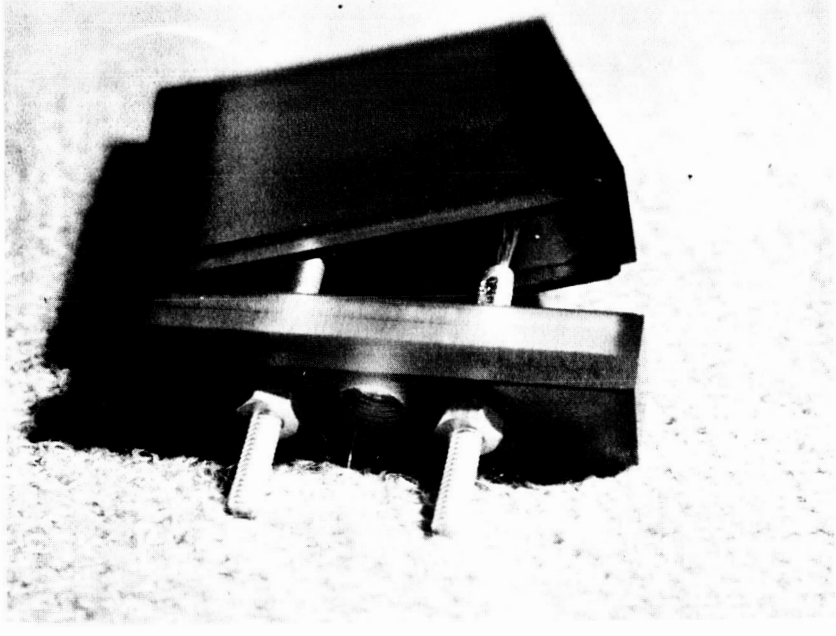
Wafer Assembly

1 Positive
2 Negatives

C2232

Figure 2. Wafer Concept





c2228

Figure 3. Case and Cover Assembly Showing One Terminal Crimped With Six Silver Wires

Polyphenylene oxide (PPO), manufactured by General Electric, is also a prime candidate material for this program and will be evaluated and compared to polysulfone. Grades under consideration are 681, 533, and 541 as coded by General Electric.

The preliminary design of case and cover is intended for testing the electrical system and establishing the sealing method.

After determining the sterilization pressures, the case and the seals will be designed with a safety margin of at least 20 to 50% over the maximum pressure ever reached during sterilization and subsequent charging of the cell.

The sealing methods to be investigated will be

(1) solvent cements,
(2) epoxy resin cements,
(3) hot gas welding, and
(4) ultrasonic welding.

The final case and cover design will be greatly dependent on the method selected.

3.6 Terminals

The terminal is made of silver-plated soft brass for low magnetic retentivity. It consists essentially of an 8-32 screw fitted into a threaded hole in the plastic cover and sealed with teflon tape. Figure 4 shows the assembly of the terminal in the cover. The terminal is screwed from the bottom until its flat median section comes to a stop.

The electrode leads are attached to the base. Figure 5 shows two variations which were tried.

Model #1: The base is slotted and partially flattened. After inserting the electrode tabs in the slot, a nut comes down and tightens the expanded section of the screw.

Model #2: The base is drilled to over 1/2 inch. The electrode leads (0.016" diameter silver wires) are inserted in the blind hole, and the base is crimped.

This design is sufficient to carry on the preliminary testing and will be improved as weaknesses develop.

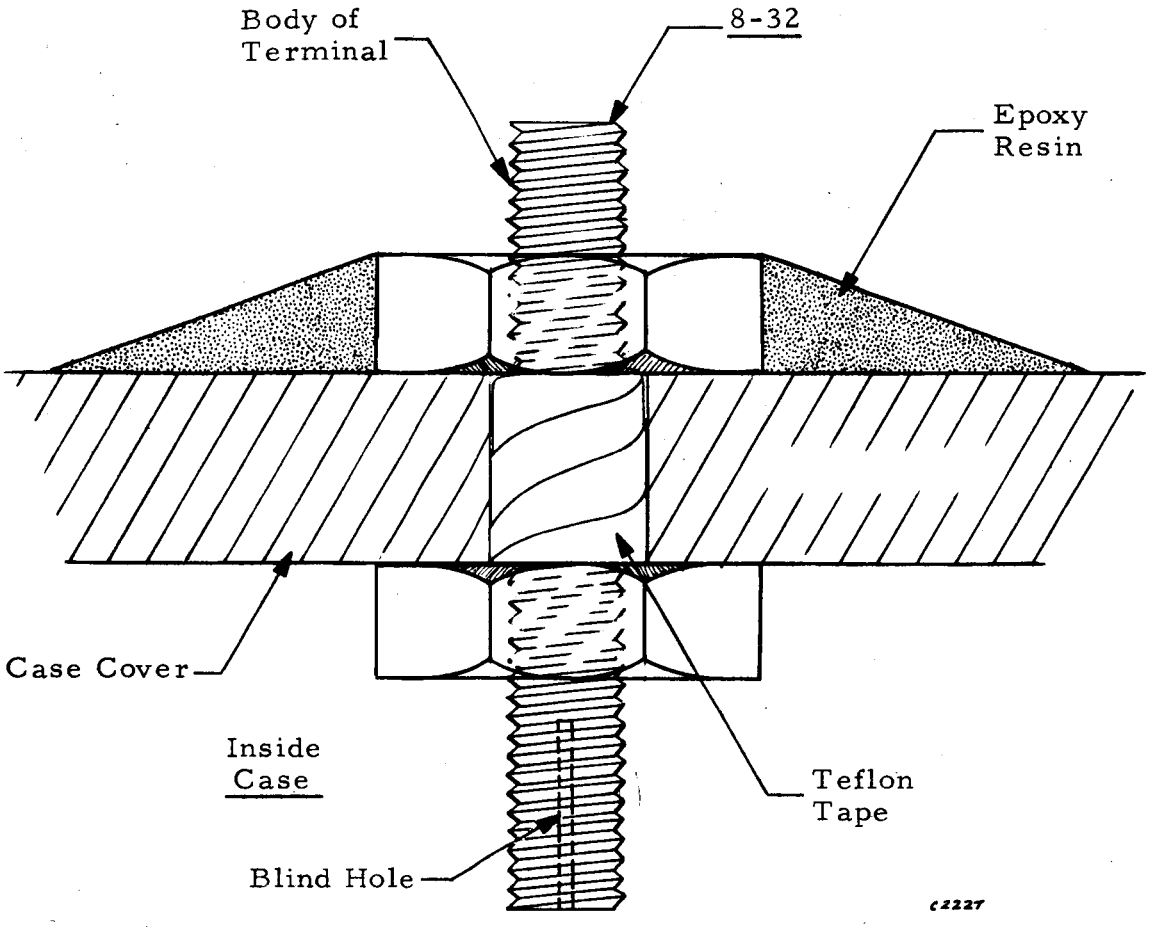


Figure 4. Terminal-to-Cover Seal Design

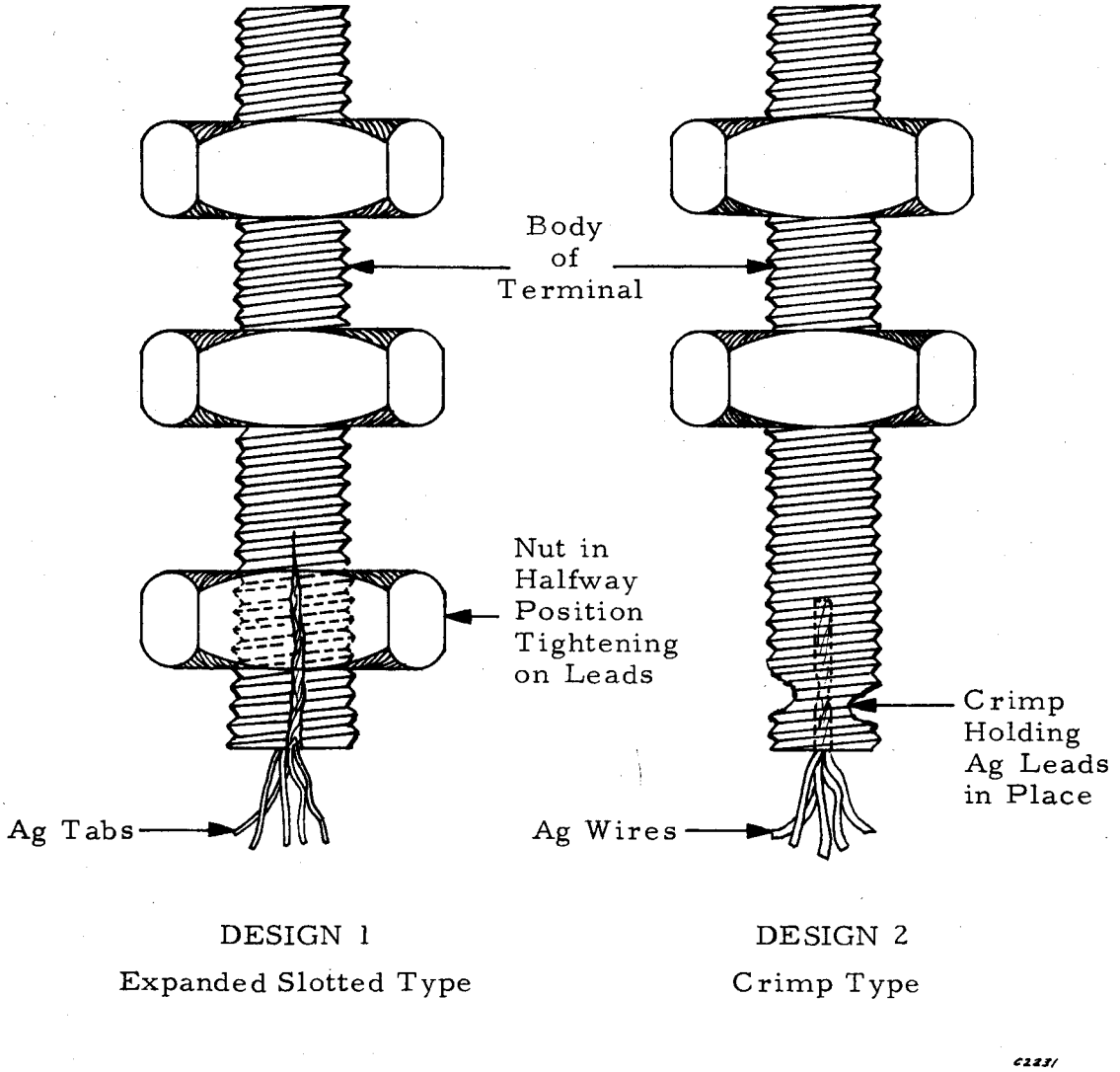


Figure 5. Attachment of Electrode Leads to Terminal

4.0 TESTING

4.1 Mechanical

4.1.1 Lead Attachment to Terminal

The electrode lead attachments to the terminal described in Section 3.6 were tested for good contact. A current of 5 A was applied through the leads up to the terminal top, and voltage drop was measured between leads and terminal top.

Model #1

	Run	Voltage
Two silver tabs 1/8 inch wide, 0.006 inch thick	1	28.5 mV
	2	30.0 mV

Model #2

Six silver .016 inch wires	1	3.2 mV
	2	4.6 mV

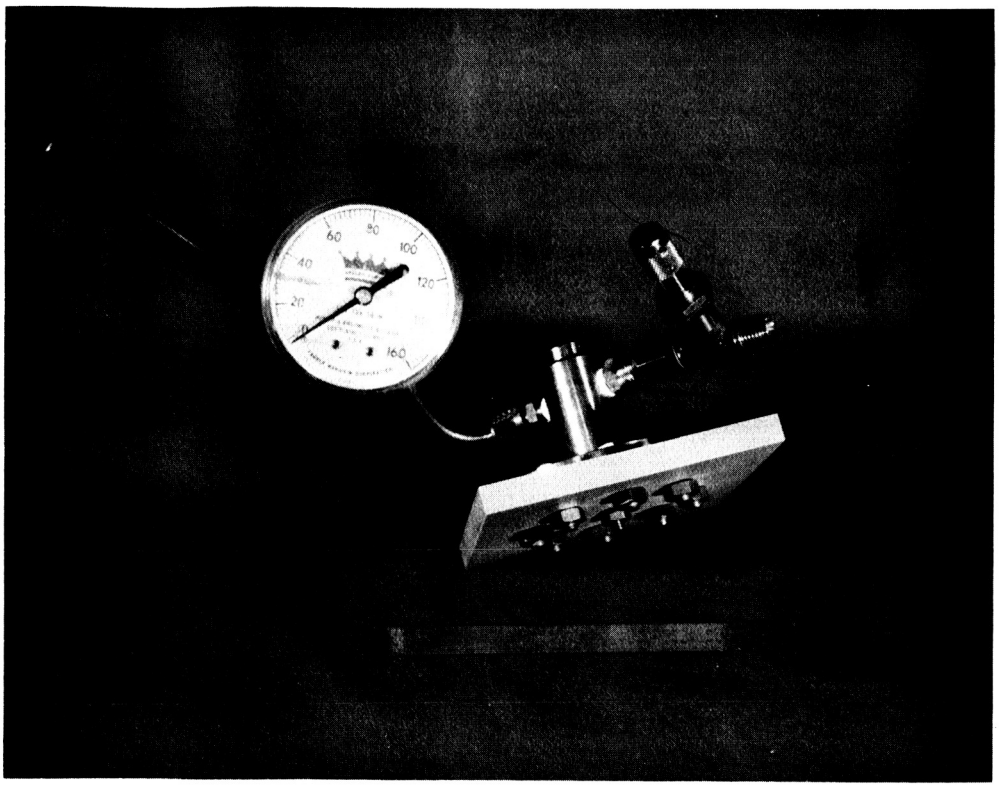
Model #2 was selected for the time being to carry on our cell assembly. Later on, a mechanical pull-out test will be devised to test quantitatively the strength of the crimp assembly. This part is left for the finalization of the design.

4.1.2 Terminal-To-Cover Seal

The terminal-to-cover seal must be gas tight at the expected test pressures and be unaffected by prolonged exposure to hot KOH.

A seal design using teflon tape to seal the terminal in the cover hole and an epoxy resin potting around the holding nut on top of the cover (see Section 3.6) was tested in a special test fixture. The fixture provided conditions more severe than those experienced during sterilization. The test fixture is shown in Figures 6 and 7.

Two terminals have been tested. Each held a pressure of 50 to 54 psig (2600 to 2800 mm Hg absolute) at 145°C for more than 108 hours (115 and 122 hours), after which the test was stopped and the terminal top checked for traces of alkali. Neither terminal had any traces.



c1347

Figure 6. Terminal Test Fixture

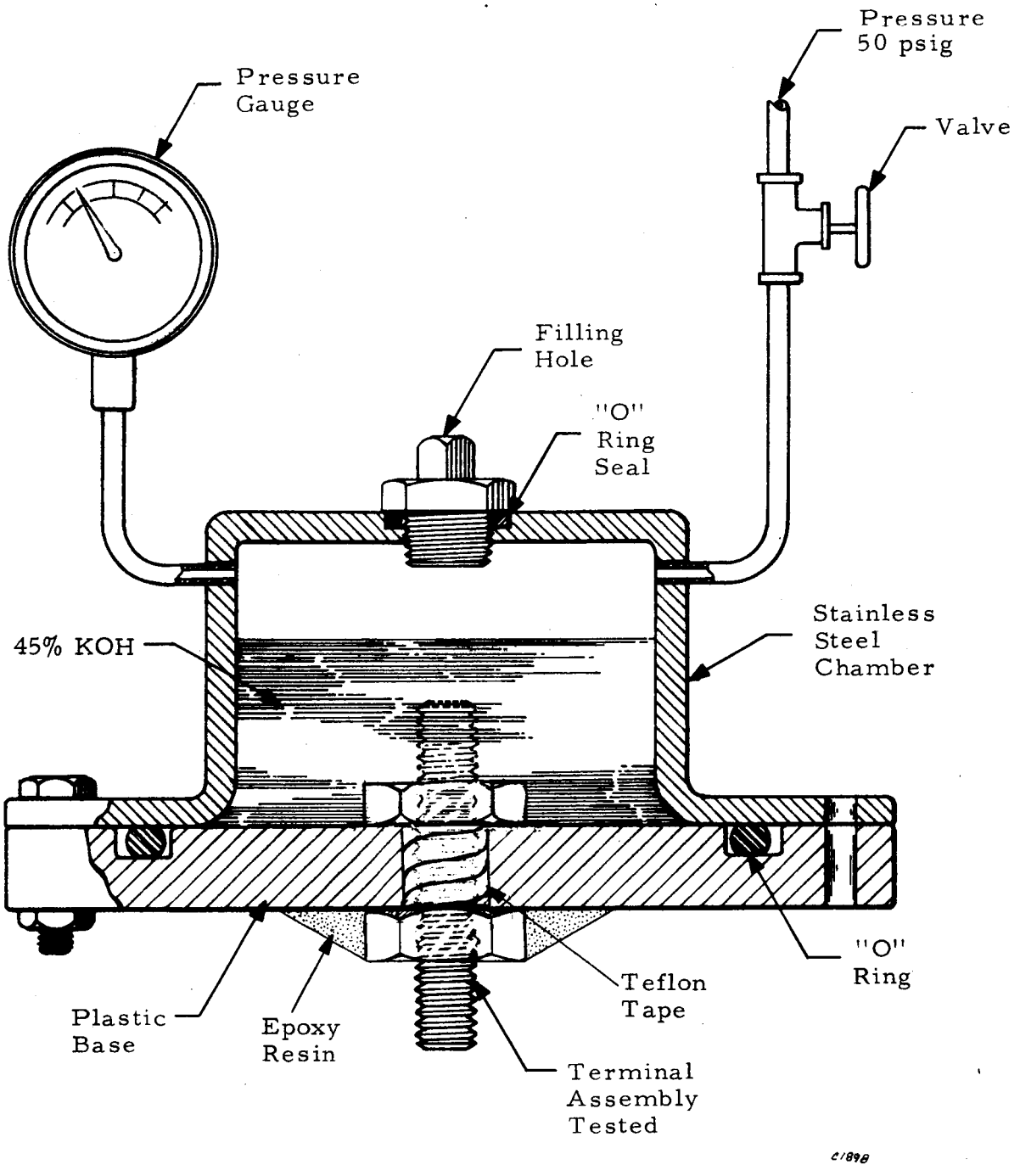


Figure 7. Schematic of Test Fixture for Terminal Seal

4.1.3 Cover-To-Case Seal

The integrity of the cover-to-case seal was tested on a few cases. The method used was the epoxy resin cementing. Two epoxy resins were selected: BR-92 (American Cyanamid Company) recommended for polysulfone; and Allbond (Allaco).

After plugging the terminal holes and sealing the cover to the case, the assembly was pressurized in increments of 10 psig, and the pressure held for five minutes. This was done at 25°C and 145°C until a leak developed or 100 psig was reached.

The procedure is considered only as a screening test. The actual test would be exposure at 145°C for 108 hours.

Below is a tabulation of the preliminary data.

	BR-92	Allbond
25°C	100 psig, 5 min. No leak	100 psig, 5 min. No leak
145°C	40 psig, 5 min. No leak 50 psig, 2 min. Pinhole leak	40 psig, 5 min. No leak 48 psig, leak 56 psig, case broke

4.2 Electrical Polarization Data

Unsterilized preliminary cell assemblies were tested electrically to verify the electrical characteristics of the cell specifications and design. Interseparators and electrolyte were the only variables; all other components were standardized to the preliminary cell design.

Interseparators tested were the following: Potassium titanate fiber sheet (KT), polyamide fiber felt (pellon), asbestos fiber sheet, treated nylon fabric (Gelman Acropor), and none, in various combinations. The electrolyte used was 30% KOH, pure or saturated with ZnO, and 45% KOH, pure or saturated with ZnO.

Polarization curves for representative cells are shown in Figure 8. Since the mission profile is 3 mA for 72 hours followed by a pulse of 2 A

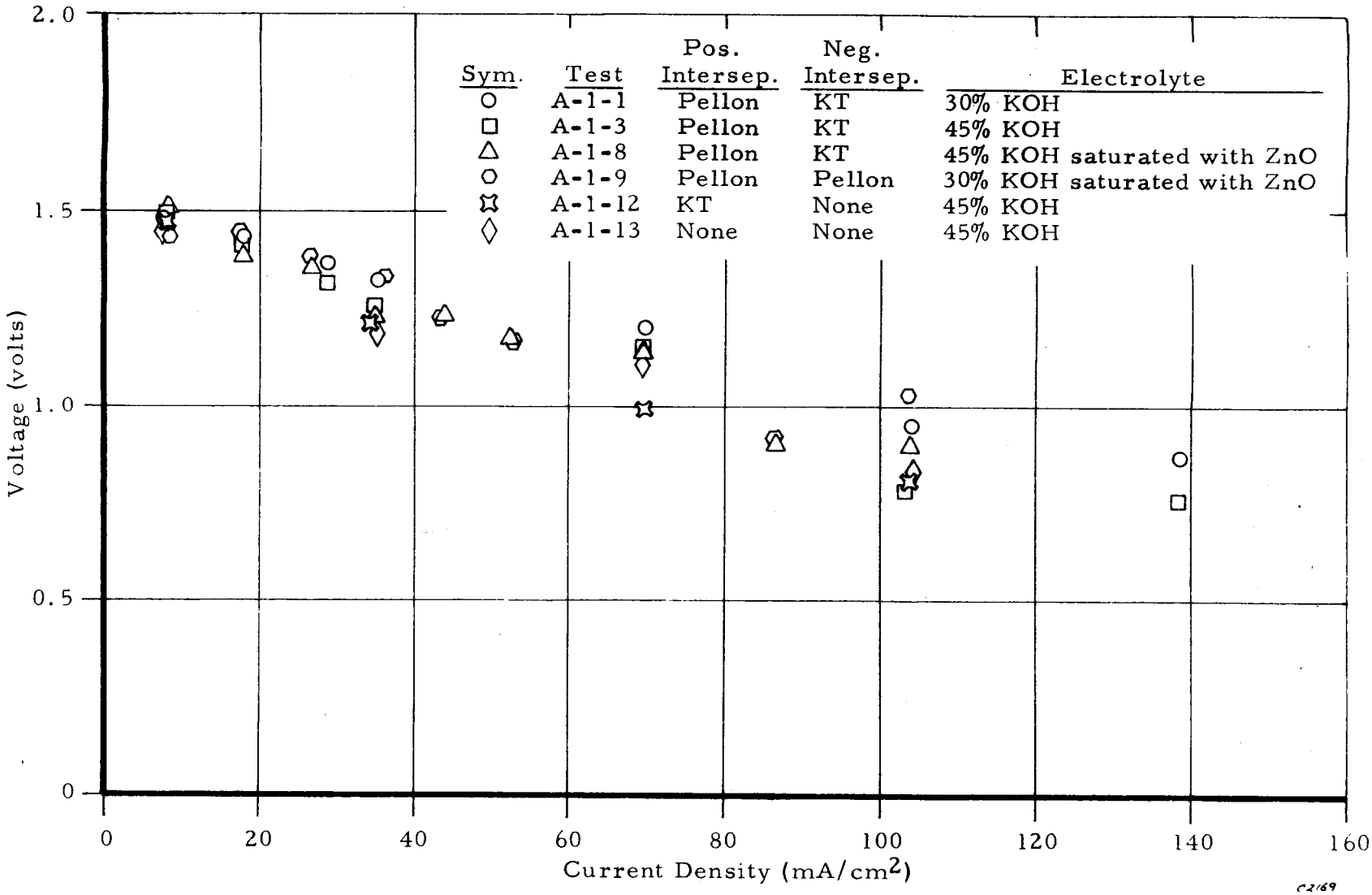


Figure 8. Polarization Curves for Representative Cells

for two minutes, the power given at the 2 A-pulse level is of importance after removal of at least an equivalent capacity (approximately 0.3 Ah). Figure 9 shows the power obtained at the 2 A pulse (current density 70 mA/cm^2) performed after discharge in excess of 0.3 Ah. It shows that electrical performance is nearly independent of the interseparator and electrolyte used, so that these may be selected on the basis of temperature and pressure considerations only.

All other cell discharges were standardized to the following regime: 0.3 A for one hour, 2 A for two minutes, then a 0.2 A drain to 1.0 V to determine the total cell capacity.

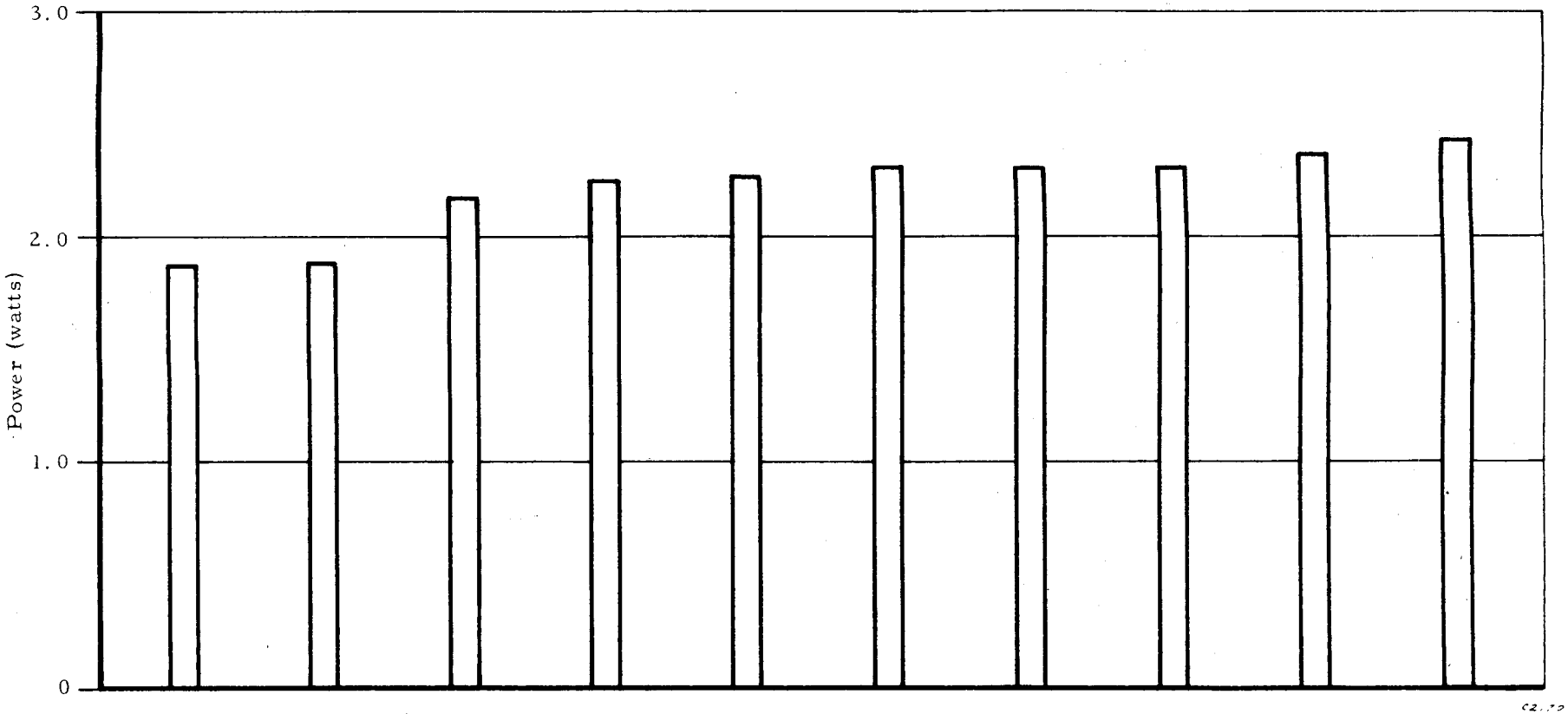
4.3 Effect of Heat Sterilization on Cell Components

A series of tests was run as a screening procedure to determine the capability of all cell components to withstand heat sterilization. To save time by quickly eliminating any component that might be adversely affected by prolonged periods in hot KOH, it was decided that a continuous 108-hour period at 145°C in an air ambient with a short temperature rise and fall period (2 to 2-1/2 hours) would be far more severe than the required three 36-hour periods in a dry nitrogen environment, with temperature rise and fall not to exceed 30°C/hour, as called out in the JPL Specification XSO-32075-TST-A of 8/24/63, modified 8/23/65.

Consequently, all individual parts were heat sterilized at 145°C for 108 hours, plus 4 to 5 hours spent during temperature rise and fall. Figure 10 shows a typical temperature profile.

After sterilization each part was examined closely and all active components were assembled with fresh counterparts and tested against controls.

The test set-up was as follows: Each item was separately placed in 30% and 45% KOH in a polysulfone case and sealed into a stainless steel pressure vessel monitored with a pressure gauge and an inside thermocouple. The pressure vessel was placed in an air-circulation drying oven and the temperature monitored to within ± 3° to 145°C. Figure 11 is a photograph of the test set-up. Each component was then evaluated separately.



Electrolyte	45% Z	45% KOH	45% KOH	45% KOH	30% Z	30% KOH	45% KOH	45% KOH	30% KOH	30% KOH
Pos. Intersep.	Pellon	KT	Gelman	Pellon	Pellon	Asbestos	None	Pellon	Pellon	Pellon
Neg. Intersep.	KT	None	None	Pellon	KT	Asbestos	None	KT	Pellon	KT

Z = Saturated zincate in indicated KOH concentration.

Figure 9. Power at the 2 A Pulse Level After Removal of 0.3 Ah

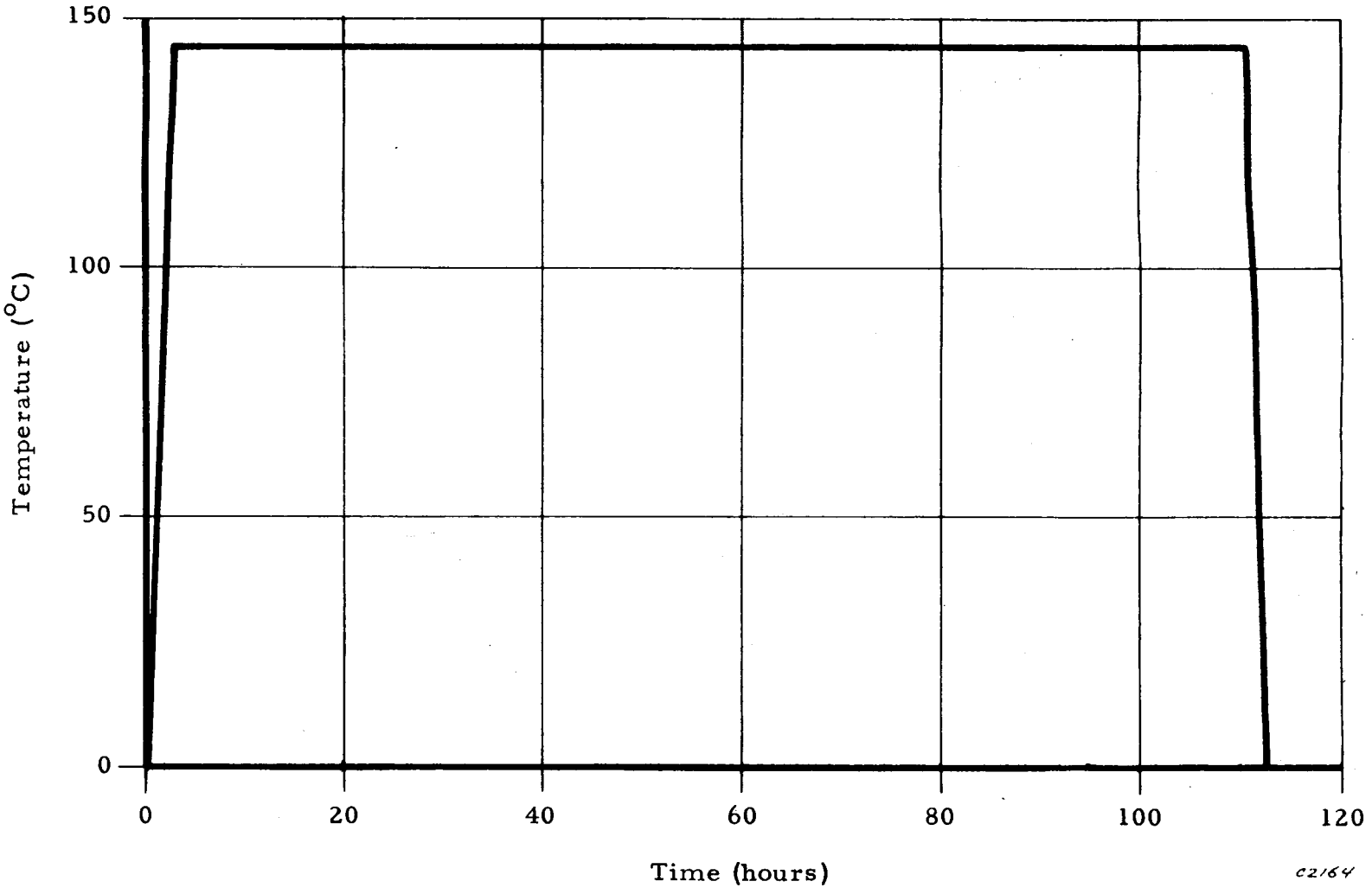
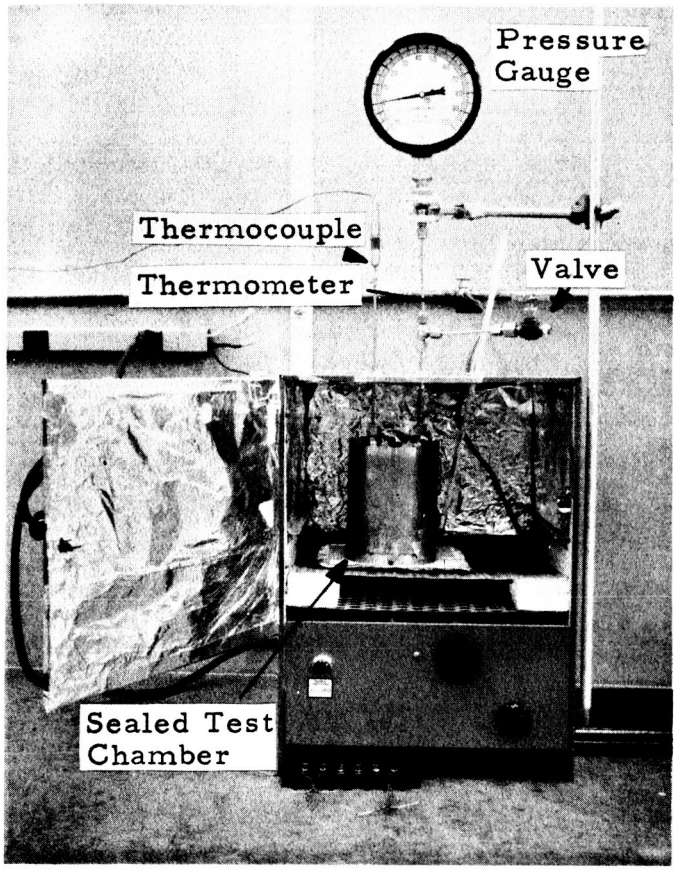


Figure 10. Heat Sterilization Temperature Profile Presently Used for Screening Tests



c2161

Figure 11. Oven Set-Up

4.3.1 Cases and Covers

Initial tests were carried out on polysulfone P-1700 to determine the compatibility of the material in 30% and 45% KOH under the heat-sterilization conditions (145°C for 108 hours).

Both molded cases (5 Ah-size) used on NASA contract NAS 3-7639 and machined cases (1 Ah-size) depicted in Figure 3 were indirectly tested. The components described in the next paragraphs were sterilized in polysulfone cases placed in sealed steel pressure chambers. This procedure allowed us to submit several cases to sterilization at the same time. No thermal degradation was observed, although some cases have spent more than 400 hours at 145°C from repeated use in different sterilization set-ups.

However, the complete assembly, case and cover fully sealed, will be retested to determine the integrity of the material and of the seals. This will also be done with the other materials mentioned in Section 3.5, when available.

4.3.2 Inorganic Separators

4.3.2.1 Manufacture

Twenty separators were selected at random from several different manufacturing batches and checked for dimensional, weight, and absorption tolerance to specifications. Table I is the result of this check. All separators were within the required tolerances.

4.3.2.2 Sterilization Test

Five of the above separators were sterilized for 108 hours at 145°C in 45% KOH, then rechecked to see if there was any change in their weight, dimension, or absorption. The results after sterilization are summarized in Table II. All figures are still within the specification tolerances. There were no significant changes in dimension, weight, density, or absorption.

4.3.3 Interseparator Materials

The materials listed in Section 3.2 were submitted to the sterilization procedure in 30% KOH, 145°C for over 108 hours.

TABLE I

TOLERANCE TO SPECIFICATIONS CHECK OF RANDOM SAMPLE OF 3420-09 SEPARATORS

	Sep. No.	Length (inches)	Width (inches)	Thickness (mils)	Volume (cc)	Mass (grams)	Apparent Density (g/cc)	% Absorption (water pickup)
Specs		2.030 ± 0.010	1.900 ± 0.010	26 ± 1	1.65 ± 0.10	4.0 ± 0.15	2.4 ± 0.25	9.5 ± 1 %
	1	2.0275	1.899	26.5	1.67	4.04	2.42	9.1
	2	2.023	1.897	26.5	1.67	4.01	2.40	9.4
	3	2.0235	1.900	26.0	1.64	3.92	2.39	9.6
	4	2.035	1.909	25.5	1.62	3.85	2.38	9.8
	5	2.032	1.903	26.5	1.68	4.03	2.40	9.4
	6	2.036	1.909	25.5	1.62	3.89	2.39	9.6
	7	2.035	1.908	25.5	1.62	3 89	2.40	9.4
	8	2.030	1.903	25.5	1.61	3.88	2.41	9.2
	9	2.030	1.905	25.5	1.62	3.87	2.39	9.5
	10	2.035	1.904	25.5	1.62	3.89	2.40	9.4
	11	2.036	1.908	26.5	1.69	4.07	2.41	9.2
	12	2.034	1.907	26.5	1.68	4.01	2.39	9.6
	13	2.032	1.905	25.5	1.62	3.91	2.41	9.2
	14	2.034	1.096	25.5	1.62	3.88	2.39	9.6
	15	2.030	1.905	25.5	1.62	3.89	2.40	9.4
	16	2.037	1.907	25.5	1.62	3.92	2.42	9.1
	17	2.034	1.905	26.5	1.68	4.00	2.38	9.8
	18	2.031	1.902	26.5	1.68	4.00	2.38	9.8
	19	2.0255	1.899	25.5	1.61	3.87	2.40	9.4
	20	2.025	1.898	26.5	1.68	4.03	2.39	9.6

TABLE II

SPECIFICATION CHECK ON FIVE RANDOMLY SELECTED SEPARATORS
HEAT STERILIZED 108 HOURS AT 145°C IN 45% KOH

	Sep. No.	Length (inches)	Width (inches)	Thickness (mils)	Volume (cc)	Mass (grams)	Apparent Density (g/cc)	% Absorption (water pickup)
Specs		2.030 ± 0.010	1.900 ± 0.010	26 ± 1	1.65 ± 0.10	4.0 ± 0.15	2.4 ± 0.10	9.5 ± 1 %
	1	2.0275	1.900	27.0	1.72	4.10	2.38	9.8
	2	2.026	1.899	27.0	1.70	3.99	2.35	10.3
	3	2.0265	1.902	26.5	1.64	3.98	2.43	8.9
	4	2.035	1.910	26 0	1.66	3.96	2.39	9.6
	5	2.034	1.905	27.0	1.71	4.08	2.39	9.6

Polyamide fiber felt (Pellon) and Gelman Acropor disintegrated upon sterilization and were deemed unsuitable.

The most promising materials are listed in Table III.

Comments: An interesting factor to consider is the capability of the material to retain KOH after the sterilization procedure. In this respect, both polypropylene SM-91 and EM-476 seemed to have increased their wettability.

KT and asbestos were still intact, but too fragile to be weighed or washed free of alkali.

Another aspect is the pressure generated during sterilization. As expected, organic materials build up higher pressure than the inorganic materials.

Also noteworthy is the fact that the polypropylene SM-91 produces quite a considerable amount of carbonation in the electrolyte.

Special Treatment: The polypropylene materials undergo a certain amount of shrinkage when immersed in KOH at 145°C. It was found to be desirable to pre-shrink them before the sterilization procedure.

The treatment consisted of a soaking in a 45%, KOH solution at 145°C for approximately 40 hours. The samples cut were carefully measured. The data are tabulated below for two samples of each material.

Material	Original Dimensions	After Treatment	After Sterilization
EM-476	27.6 cm^2 27.0 cm^2	25.0 cm^2 25.2 cm^2	13.40 cm^2 14.70 cm^2
SM-91	26.80 cm^2 25.75 cm^2	23.25 cm^2 22.10 cm^2	23.25 cm^2 22.10 cm^2

After treatment, EM-476 shrank by 7 to 9% and SM-91 by 13 to 14%.

TABLE III

INTERSEPARATOR MATERIALS STERILIZED IN 30% KOH

Material	KOH Absorption Before Test	Hours At 145°C	Maximum Pressure In Vessel mm Hg	KOH Absorption After Test	Carbonation of Electrolyte	% Area Shrunk
Polypropylene SM-91 pre-shrunk	15 mg/cm^2	113	3290	30 mg/cm^2	considerable	0
Polypropylene EM-476 pre-shrunk	9 mg/cm^2	114	3500	16 mg/cm^2	slight	44%
Potassium Titanate Sheet (KT)	F	111	1330	F	slight	0
Asbestos Sheet	48 mg/cm^2	113	2260	F	none	0
Coating 4561-7 on Ag Plate	Not fully evaluated at the time of this writing.					

F = Intact, but too fragile for measurement

After sterilization and comparing to the new post-treatment area, the shrinkage percentage was respectively 48% and 0%.

The physical appearance also showed a difference: whereas the EM-476 became quite stiff, the SM-91 remained soft and flexible.

The SM-91 propylene will be retained as a candidate for further testing.

4.3.4 Sealants

This section deals exclusively with the problem of finding a sealant suitable for bonding the inorganic separators placed on either side of the zinc electrode, thus encapsulating the electrode and making a wafer element as depicted in Figure 2.

Several sealants tested at room temperature in concentrated KOH solution maintained the integrity of the seal for a long time without apparent degradation or chemical attack. At 100°C and higher, the integrity of the seal is a function of the length of time of exposure to alkali and, depending on the material, may vary from days to months. Therefore, it was important to determine if there would be a sufficiently good retention of the seal at the sterilization conditions.

The sealants per se were tested in 45% KOH at 145°C for 108 hours in pressure vessels. They were

1. Unichrome U-218X (M&T Chemicals, Inc.)
2. Chem-O-Sol PK4706 (Plas-Kem Corp.)
3. Uralane (Furane Plastics, Inc.)
4. RTV-102 (G.E.)
5. Si-O-Flex SS-831 (Stauffer Chemicals Co.)
6. Allbond epoxy resin (Allaco).

The first five broke down. Allbond did not show shrinkage or chemical breakdown to any great extent. All preliminary work on negative wafers have been made with it. New methods of applying the resin and new techniques of curing at very high temperatures are being tried to improve its resistance to KOH.

Allbond, when not directly exposed to alkali such as during potting the terminals, has given excellent results and has been used exclusively so far.

4.3.5 Silver Electrodes

Unformed sterilized silver electrodes show no visible evidence of any changes due to heat sterilization. The ability to accept charge, the maintenance of open circuit voltage, and discharge capacity were well within the expected performance range of unsterilized control plates, after the sterilized plates were assembled against unsterilized components. Figure 12 shows discharge curves of a sterilized silver electrode and of an unsterilized control.

4.3.6 Negative Wafers

Negative wafers made by sandwiching a negative electrode between two inorganic separators and sealing, in this case with an epoxy resin, showed no effect from the heat sterilization except a tendency for the ZnO to boil out through the small filling hole in the top of the wafer. The loss was small but will be eliminated in the future by packing the top of the wafer with Armalon felt before sealing. Previous experience has proven this to be very effective in containing the ZnO. The Allbond sealant was slightly attacked but continued to hold its bond.

Figure 13 shows discharge curves of a sterilized negative wafer assembled with unsterilized counterparts and of an unsterilized control. The capacity obtained is comparable to that of the unsterilized wafer, but there is some degradation of the voltage plateau.

4.3.7 Pressure Determination

4.3.7.1 Approach Philosophy

The pressure in the sealed cell during heat sterilization is caused mainly by the water vapor pressure of the alkali solution, the expansion of gases caused by the elevation of temperature, and by gas evolution caused by chemical processes (dissolution of material in electrolyte, reduction, local actions, etc.). If the active materials are taken in their original form (pure silver and pure zinc oxide) the amount of gas

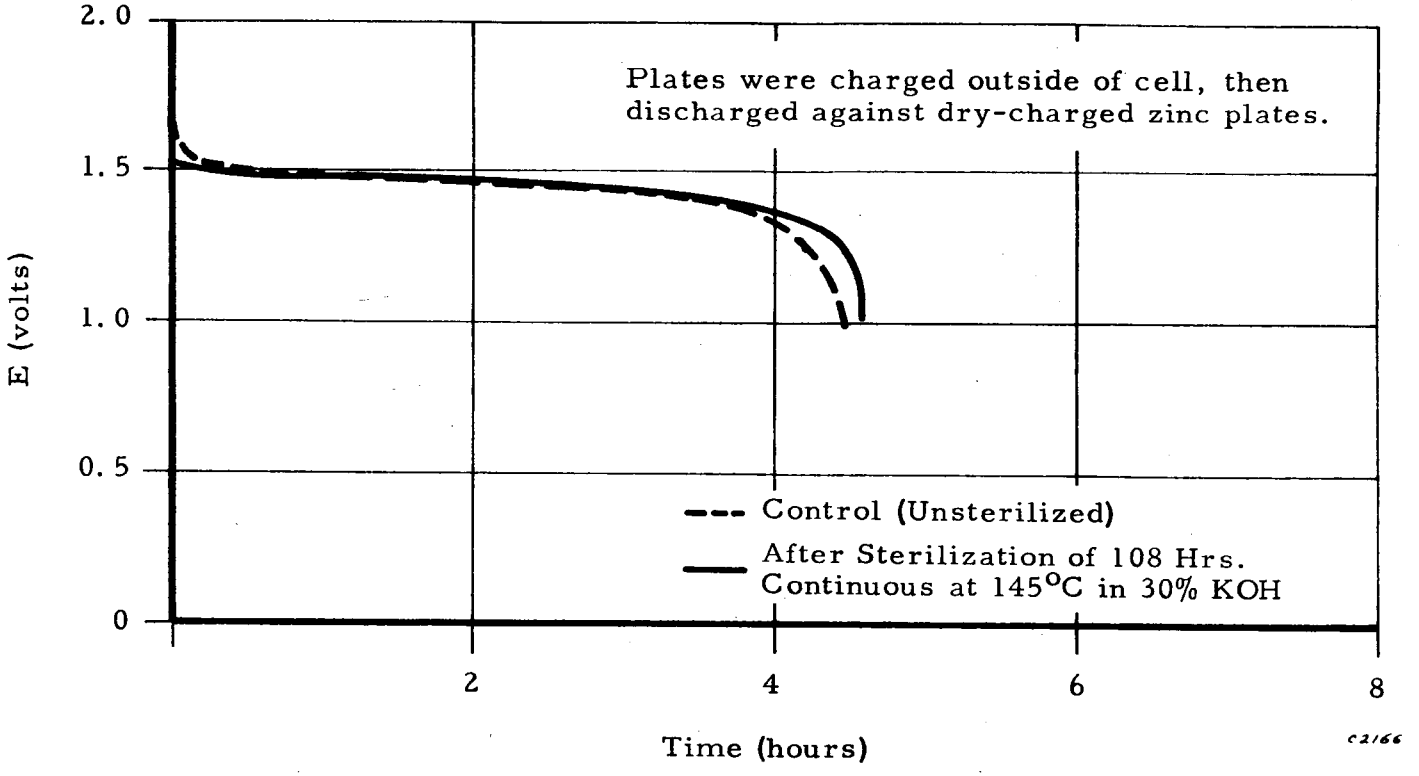


Figure 12. Discharge of Silver Plates at 300 mA (Current Density 10 mA/cm^2)

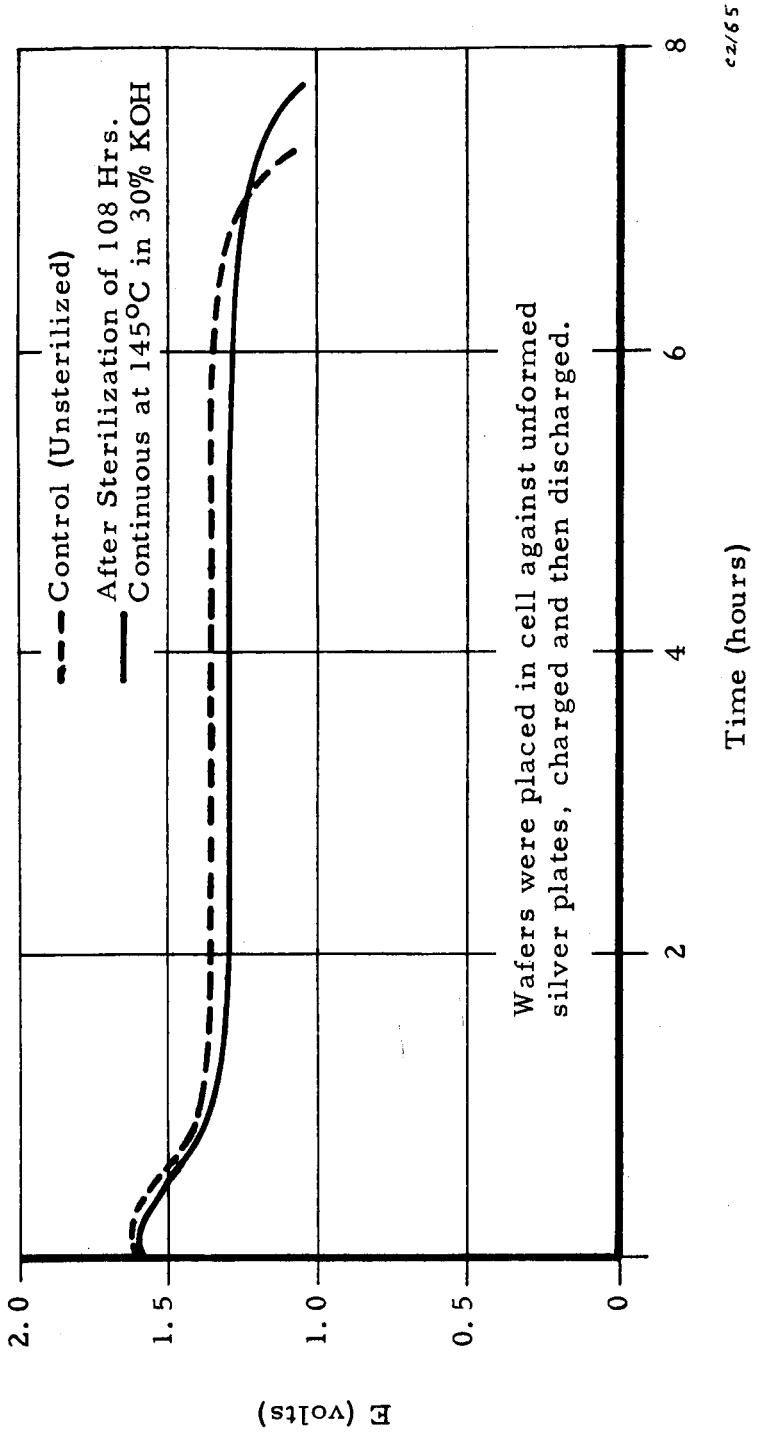


Figure 13. Discharge of Negative Wafers at 300 mA (Current Density 10 mA/cm^2)

evolved due to chemical action is practically nil and can be measured to verify it. The pressure caused by temperature rise can be minimized if maximum evacuation of the cell is done at room temperature before sealing.

The main factor, then, is the vapor pressure. It is known that at a given temperature the vapor pressure decreases as the KOH concentration increases. This compels us to consider the two extreme concentrations, 30% and 45%, with relation to pressure and electrical performance and establish the optimum point on the basis of trade-off.

Figures 14 and 15 give data on KOH pressure against temperature at various concentrations.

Since ZnO dissolves readily in KOH at high temperature, it is possible that the vapor pressure of a saturated zincate solution of 45% KOH may even yield a lower pressure. Consequently, our tests utilize this type of electrolyte as well.

Another consideration is the relative succession of the sterilization procedure and the cell formation procedure; which one must precede is a matter of experimentation rather than of judgment, since the order of procedures is debatable.

On one hand, the sealed cell, when still unformed, will develop relatively low pressures only of the order of magnitude of the KOH vapor pressures at 145°C. The active materials sterilized in their original raw form are not expected to degrade, so that after sterilization the cell can be submitted to a regular formation, which is nothing more than a normal charge and discharge cycle.

On the other hand, starting with the formation would establish the cell performance and eliminate any possibility of fabrication deficiency before the cell is sealed and delivered to be mounted on the spacecraft and submitted to sterilization. However, after the formation discharge, the zinc electrode does not return to its original state of zinc oxide and mercuric oxide. At the sterilization temperature, the zinc electrode may undergo more degradation and therefore evolve hydrogen profusely. This approach must be tested to determine the extent of the degradation and the pressure build-up.

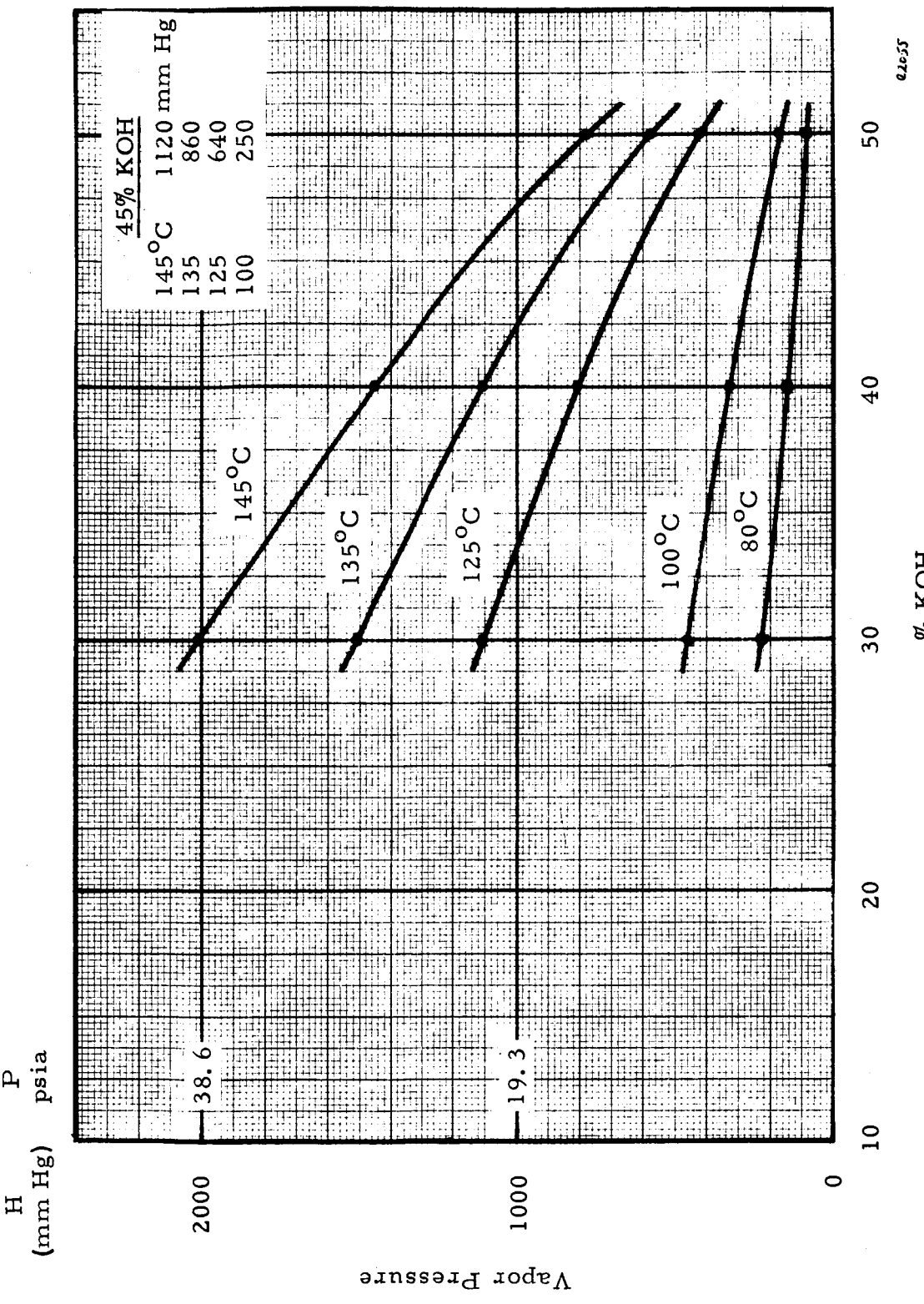


Figure 14. Vapor Pressure of KOH

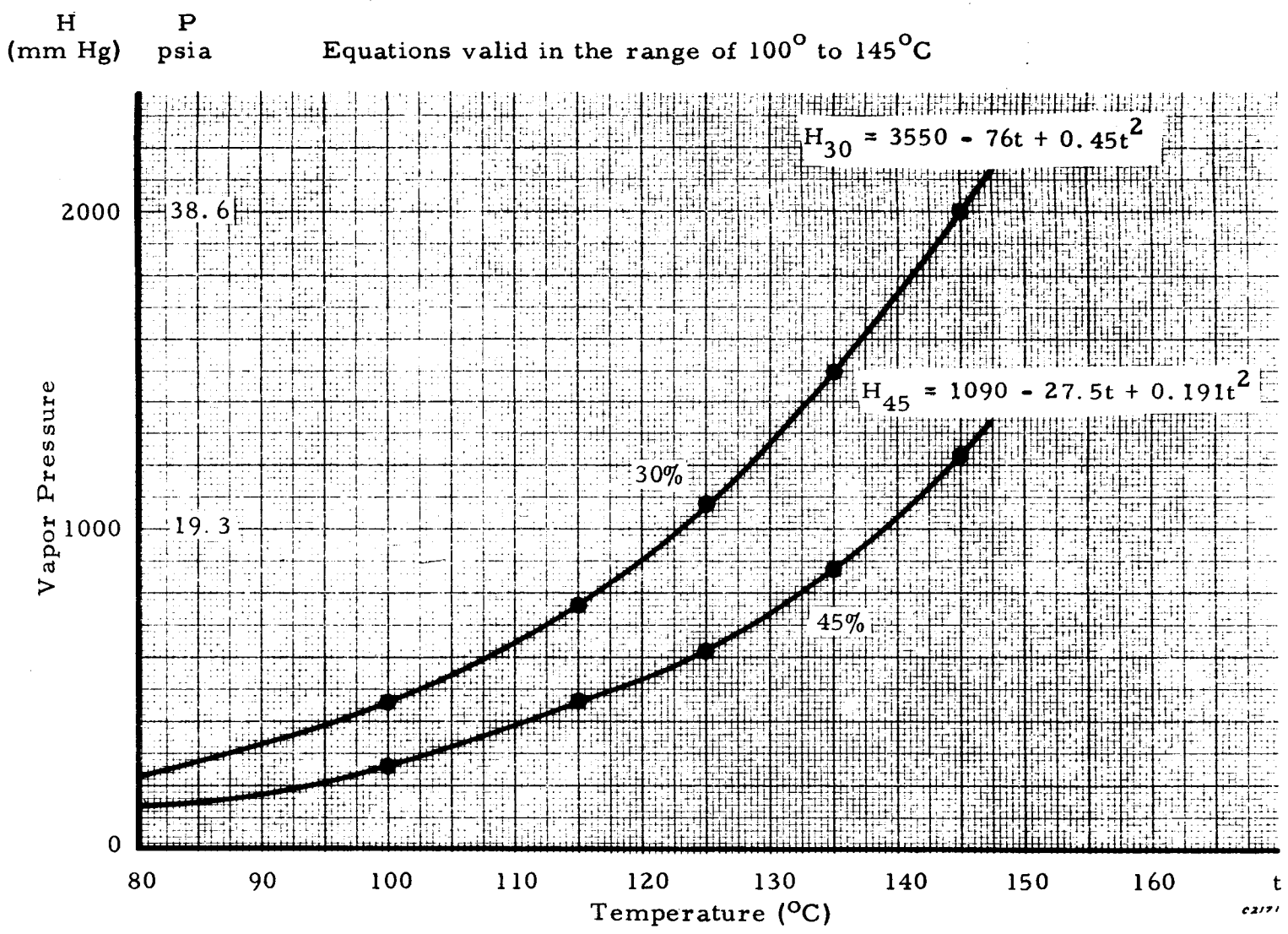


Figure 15. Vapor Pressure of KOH

Cells will be evaluated side by side, formation following sterilization and vice-versa.

4.3.7.2 Pressure Determination

Tests carried out on cell components being sterilized were also intended to determine the range of pressures to be encountered during the sterilization procedure from all sources: vapor pressures, gas expansion caused by elevated temperature, gas evolution caused by chemical processes or degradation.

The tests also serve to determine how much of a reduction in pressure can be expected by using 45% KOH over 30%, and by using zincate (KOH saturated with ZnO) rather than pure KOH solution.

The contribution of each cell component, alone or in combination, to pressure rise at 145°C is determined while they are undergoing regular sterilization experiments. The time spent at 145°C varies from a short time after the pressure stabilizes (approximately 3 hours) to full length test procedure (108 hours).

Table IV lists the pressures obtained for each component in different electrolytes. Table V categorizes them by electrolyte type.

Most promising candidates are listed with their maximum pressures in Figure 16.

The pressure obtained is not entirely predictable in nature because of the partial pressures other than vapor pressure (see Section 4.3.8).

Most of the tests were started at atmospheric pressure with ambient air sealed in the vessel. The pressure reaches a peak at 145°C throughout the sterilization time; at the end, upon cooling off, the pressure drops and does not necessarily return to atmospheric. It may be higher, due to generation of new gases or lower due to oxygen dissolution in electrolyte or oxidation of organic materials by available oxygen. The gas analysis in one instance (see Section 4.3.8) shows a drastic diminution of the oxygen content (from 21% in the original ambient down to 3%)

TABLE IV

PRESSURES CATEGORIZED BY COMPONENTS

Item	Electrolyte	Pressures (mm Hg Absolute) Start @ 25°C	Peak @ 145°C	End @ 25°C	Gas Sample
Unformed Silver Electrode	45%-Z	760	1690	*	
	45% KOH	760	1900	*	
	30%-Z	760	2620	*	
	30% KOH	760	2670	*	
Negative Mix A	45%-Z	760	2050	*	
	30%-Z	760	2830	*	
Unformed Silver Electrode and ZnO	45%-Z	760	2050	*	
	30%-Z	760	2620	*	
3420-09 Separator	45%-Z	760	1430	630	
	45%	760	2210	*	X
	30%-Z	760	2620	630	
Unf. Silver Electrode ZnO & 3420-09 Sep.	45%-Z	760	2210	*	
	30%-Z	760	3140	*	
Allbond Sealant	45% KOH	760	1790	*	X
Potassium Titanate Fiber Sheet (KT)	45% KOH	760	2310	*	X
	30% KOH	760	1330	*	X
Asbestos Fiber Sheet	45% KOH	760	2210	*	X
	30% KOH	760	2260	*	X
Polypropylene SM-91	45% KOH	760	2360	*	X
	30% KOH	760	3290	*	X
Polypropylene EM-476	45% KOH	760	2050	*	X
	30% KOH	760	3500	*	X
Wafer with Dummy Electrode, Allbond Sealant	45%-Z	760	2470	*	
	30%-Z	760	2310	*	
Negative Wafer Allbond Sealant	45%-Z	760	1850	510	
	30%-Z	760	3090	630	
	30% KOH	760	3600	*	X

*No end pressure was noted because the chamber was opened before complete return to ambient temperature.

Z = KOH saturated with ZnO

TABLE V

PRESSURES CATEGORIZED BY ELECTROLYTE

Electrolyte	Item	Pressures (mm Hg Absolute) Start @ 25°C	Peak @ 145°C	End @ 25°C	Gas Sample
45%-Z	Unformed Silver Electrode	760	1690	*	
	Negative Mix A	760	2050	*	
	Unformed Silver Electrode & ZnO	760	2050	*	
	3420-09 Separator	760	1430	630	
45%-Z	Unformed Silver Electrode, ZnO & 3420-09 Separator	760	2210	*	
	Wafer with Dummy Electrode — Allbond Sealant	760	2470	*	
	Negative Wafer — Allbond Sealant	760	1850	510	
45% KOH	Unformed Silver Electrode	760	1900	*	X
	3420-09 Separator	760	2210	*	X
	Allbond Sealant	760	1790	*	X
	Potassium Titanate Fiber Sheet (KT)	760	2310	*	X
	Asbestos Fiber Sheet	760	2210	*	X
	Polypropylene SM-91	760	2360	*	X
	Polypropylene EM-476	760	2050	*	X
30%-Z	Unformed Silver Electrode	760	2620	*	
	Negative Mix A	760	2830	*	
	Unformed Silver Elec. & ZnO	760	2620	*	
	3420-09 Separator	760	2620	630	
	Unf. Silver Electrode, ZnO & 3420-09 Separator	760	3140	*	
	Wafer with Dummy Electrode — Allbond Sealant	760	2310	*	
	Negative Wafer — Allbond Sealant	760	3090	630	
30% KOH	Unformed Silver Electrode	760	2640	*	
	Potassium Titanate Fiber Sheet (KT)	760	1330	*	X
	Asbestos Fiber Sheet	760	2260	*	X
	Polypropylene SM-91	760	3290	*	X
	Polypropylene EM-476	760	3500	*	X
	Negative Wafer — Allbond Sealant	760	3600	*	X

*No end pressure was noted because the chamber was opened before complete return to ambient temperature.

Z = KOH saturated with ZnO

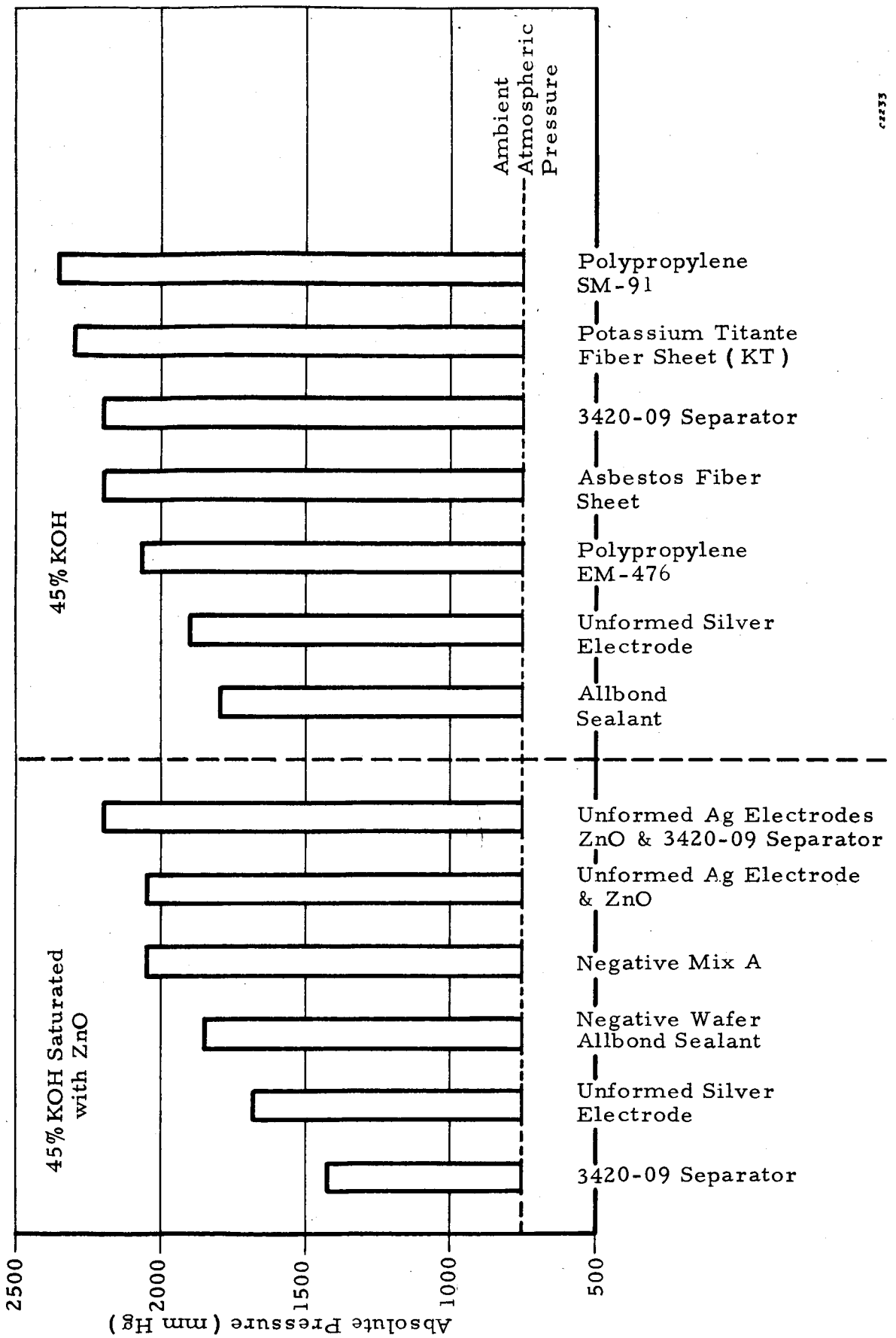


Figure 16. Pressures Generated by Most Promising Cell Components

while the nitrogen content goes up to 92%. This discovery leads naturally to the idea of flushing the cell with oxygen before sealing, thus removing all nitrogen, or else simply evacuating the cell to the maximum before sealing. It will be possible to reduce the maximum pressure to a level close to the vapor pressure of the electrolyte being used.

4.3.8 Gas Analyses

The sealed vessels where the components are sterilized are provided with valves. At the end of the sterilization, samples of the internal gas mixture can be obtained through the valves by means of a special syringe. The gas mixture sample is injected in a gas chromatograph and analyzed qualitatively and quantitatively. Organic gases were detected by means of an I-R spectrophotometer. Several gas analyses were performed. At the same time, sterilized electrolyte was checked for carbonation.

Table VI gives the gas analyses for only some selected components which are worth considering.

Selection of the best sterilizable components must be based on minimum hydrogen evolution, minimum carbonation, and minimum pressure. However, diminution of oxygen pressure is often connected with heavy carbonation. A trade-off may be necessary. More tests must be run before making a full assessment of the gas analysis data.

TABLE VI

RESULTS OF GAS ANALYSES ON SELECTED COMPONENTS

Material	Time @ 145°C	N_2 %	O_2 %	H_2 %	CO_2 %	CO %	CH_4 %	H_2O Vapor %	Misc. Gases %	Electrolyte Carbonation
Polysulfone Case	36 hrs.	80.2	18.4	—	trace	—	—	trace	1.4	—
	108 hrs.	80.0	16.0	—	—	trace	—	trace	4.0	slight
3420-09 Separators	112 hrs.	83.0	16.0	—	trace	—	1.0	trace	—	considerable
Cured Allbond Sealant	18 hrs.	92.0	3.0	3.0	trace	—	2.0	trace	traces	considerable
Potassium Titanate Fiber Sheet (KT)	41 hrs.	83.0	16.0	—	trace	trace	trace	trace	traces	slight
Asbestos Fiber Sheet	113 hrs.	81.0	16.0	2.0	trace	—	1.0	trace	—	none
Polypropylene EM-476 - pretreated	114 hrs.	80.0	20.0	—	trace	—	trace	trace	—	slight
Polypropylene SM-91 - pretreated	113 hrs.	84.0	16.0	—	trace	—	—	trace	—	considerable

5.0 SUMMARY

The first quarter was devoted mainly to study of component contribution to pressure and gas composition during the sterilization procedure. Several tests on silver and zinc oxide electrodes, separators and interseparators, sealants, and combinations in various electrolytes gave pressures as high as 3600 mm Hg absolute and as low as 1400 mm Hg. The gas analysis generally showed a typical decrease in oxygen content, very little hydrogen, and organic gases at times up to 5% (mainly methane).

Design and development of mechanical hardware — terminal, case, cover — are progressing.

Preliminary tests were performed on fabricated parts and deemed satisfactory for subsequent electrical testing and development of sealing method. However, improvement of these parts must be carried out concurrently until their reliability is established.

6.0 WORK PLANNED

In the next quarter, it is planned to

(1) continue our study of pressure and gas composition,

(2) establish the best sealing method for the cover-to-case assembly, and

(3) gather electrical data on assembled cells submitted to sterilization.